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(54) Title of the Invention: Method of manufacturing a highly durable separable fastener

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fastener

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1. Title of the invention

Method of manufacturing a highly durable separable fastener

2. What is claimed is:

- (1) A method of manufacturing a separable fastener, wherein a separable fastener comprising synthetic fibers is back-coated with a two-solution curing type polyurethane aqueous dispersion element, wherein a highly durable separable fastener is obtained by using (A) a polyurethane aqueous dispersion element obtained using polytetramethylene glycol having an average molecular weight of 300-3000 as principal reagent, an organic diisocyanate, a carboxyl group-containing compound and a tertiary amine as principal starting materials, and (B) a water-soluble compound having two or more epoxy rings or aziridine rings in the molecule as curing agent.
- (2) The manufacturing method as described in Claim 1, wherein the average molecular weight of the polytetramethylene glycol is 400-1500.
- (3) The manufacturing method as described in Claim 1 or 2, wherein the organic diisocyanate is an aliphatic or alicyclic diisocyanate.
- (4) The manufacturing method as defined in any of Claims 1 to 3, wherein the carboxyl group-containing compound is an  $\alpha, \alpha$ -dimethylol alkane acid.
- (5) The manufacturing method as defined in any of Claims 1 to 4, wherein the tertiary amine is a trialkylamine.
- (6) The manufacturing method as defined in Claim 5, wherein the trialkylamine is trimethylamine or triethylamine.
- (7) The manufacturing method as defined in any of Claims 1 to 5, wherein the tertiary amine is a dialkyl monoalkylamine or a monoalkyl dialkanolamine.
- (8) The manufacturing method as defined in any of Claims 1 to 7, wherein, in the polyurethane aqueous dispersion element (A), the amount of carboxyl introduced in the polyurethane and which forms a salt with the tertiary amine is 0.8-3.0 weight parts relative to polyurethane.
- (9) The manufacturing method as defined in any of Claims 1 to 8, wherein hydrazine or a dihydrazide is used as a chain extending agent in the manufacture of the polyurethane aqueous dispersion element.

(10) The manufacturing method as defined in any of Claims 1 to 9, wherein the usage proportion of curing agent is 2-20 weight parts relative to 100 weight parts of the base resin in terms of solids.

### 3. Field of the Invention

#### Industrial Applicability

This invention relates to a method of manufacturing a separable fastener having excellent performance using an aqueous dispersion element which presents no problem from the viewpoint of safety and environmental pollution.

#### Prior Art

In the past, separable fasteners typically comprised a woven fabric (sheet) having plural hooks or pieces of identical function shaped for example like mushrooms (hereafter, referred to as hooks) on a surface, and a woven fabric (sheet) having plural loops or pieces of identical function on a surface (hereafter, referred to as loops), the two sheets being joined together by the engaging of the hooks and loops. This separable fastener can be fastened and unfastened as desired, and is used as a universal means of fastening in a wide range of applications such as shoes, seat covers or the like.

This separable fastener is generally manufactured by implanting the hooks and loops into a woven fabric (sheet), an organic solvent solution of a resin or an aqueous dispersion element is coated onto the undersurface, i.e. the undersurface of the separable fastener in order to prevent the pile from fraying due to repeated fastening and unfastening, and fix the fastener. Then, the woven fabric (sheet) is attached to a base material such as a cloth (woven or unwoven), leather, or a plastic sheet such as PVC by sewing, sticking with adhesive or by high frequency adhesion. The resin used is conventionally a resin such as polyurethane, polyester or polyimide, however polyurethane comprising a polyol such as polyethylene adipate, polybutylene adipate, polypropylene glycol, poly tetramethylene glycol or polyhexamethylene glycol together with an organic diisocyanate has recently come into wide use on account of its performance.

Problems which this invention attempts to solve

However, separable fasteners comprising the above polyurethane as back coating often had severe fraying of the pile after repeated fastening and unfastening over long periods, or washing and dry cleaning, and this led to spoiling of the appearance. In addition, there was an increased decline of bonding force between the hooks and the loops, so a method of improving this was desired.

The polyurethane used as a back coating for separable fasteners as described above was in the form of an organic solvent solution or aqueous dispersion element, but in the case of an organic solvent solution there were serious problems as regards hygiene and environmental pollution. On the other hand, in the case of an aqueous dispersion element, there was considerable loss of performance of the separable fastener necessarily due to the fact that it had greater hydrophilic properties than the organic solvent type, and there were problems with regard to washability and tolerance to dry cleaning.

It is therefore an object of this invention to provide a method of manufacturing a separable fastener using polyurethane in the form of an aqueous dispersion element which presents no problem regarding safety, hygiene and environmental pollution, which fixes the pile of the separable fastener, and which has long-term durability insofar as there is very little fraying of pile due to violent, repeated fastening and unfastening, washing or dry cleaning.

Means to solve the problems

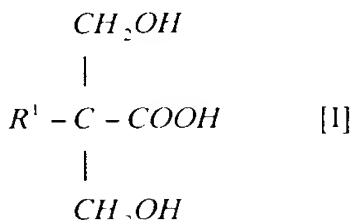
According to this invention the above object is obtained by a method of manufacturing a separable fastener wherein a separable fastener formed of synthetic fibers is back coated with a two-solution type curing polyurethane aqueous dispersion element (A), using polytetramethylene glycol having an average molecular weight of 300-3000 as principal reagent, an organic diisocyanate, a carboxyl group-containing compound and a tertiary amine as principal starting materials, and (B) a water-soluble compound having two or more epoxy rings or aziridine rings in the molecule as curing agent.

The average molecular weight of the polytetramethylene glycol used to manufacture the polyurethane aqueous dispersion element which is the base resin in this invention, is 300 to 3000, and preferably 400-1500. If this range is not respected, and the dispersion element is used as a polyurethane aqueous dispersion element for back coating the separable fastener, the separable fastener has inferior durability to fluffing, washing and dry cleaning, and its appearance is also unattractive.

The organic diisocyanate used in the manufacture of the above aqueous dispersion element in this invention may be an aliphatic, alicyclic or aromatic organic diisocyanate known in the art having two isocyanate groups in the molecule. Examples are isophorone diisocyanate, hexamethylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, hydrogenated xylene diisocyanate and cyclohexane diisocyanate, but aliphatic or alicyclic organic diisocyanates, e.g., isophorone diisocyanate or hexamethylene diisocyanate, are particularly to be preferred as their use gives a separable fastener with excellent durability to fluffing and washability in this invention.

In the manufacture of the polyurethane aqueous dispersion element, the molar ratio of organic diisocyanate to polytetramethylene glycol of average molecular weight 300-3000 is normally in the range 1: 1.5-1: 6, but preferably 1: 2-1: 5. The optimum composition within the above range may be chosen according to the molecular weight of the polytetramethylene glycol.

The carboxyl group-containing compound used in the manufacture of the aqueous dispersion element of this invention may be a compound containing at least one carboxyl group and at least two groups containing an active hydrogen atom excluding carboxyl, for example hydroxyl or amino groups, but dihydroxyl group-containing alkane acids are to be preferred. Of dihydroxyl group-containing alkane acids, a dimethylol alkane acid having the general formula:



is preferred. Here,  $R^1$  is hydrogen or an alkyl group, but preferably an alkyl group having 1-5 carbon atoms. Specific examples of  $\alpha$ - $\alpha$  dimethylol alkane acids are 2,2-dimethylol propionic acid, 2,2-dimethylol acetic acid, 2,2-dimethylol butanic acid and 2,2-dimethylol pentanoic acid, but 2,2-dimethylol propionic acid is particularly preferred.

The carboxyl group in the carboxyl group-containing compound has less reactivity to isocyanate groups than hydroxyl groups or amino groups in the compound, and has almost no reactivity with organic isocyanates during the manufacture of the aqueous dispersion element. The carboxyl group-containing compound and organic diisocyanate selectively react between isocyanate groups and hydroxyl or amino groups, and give a polymer structure having a dangling carboxyl group which can be used to form a tertiary amine and a quaternary salt. In the manufacture of the polyurethane aqueous dispersion element, the carboxyl group introduced into the polyurethane is neutralized by the tertiary amine used to manufacture this aqueous dispersion element, and an excellent polyurethane aqueous dispersion element is thus obtained. The content of carboxyl groups, i.e.,

ionized carboxyl groups ( $-\overset{0}{C}\overset{0}{-}O^0$ ) is 0.8 percent-3.0 wt%, but preferably 1.0-2.0 wt%, in terms of polyurethane solids. It is undesirable that this content is less than 0.8 wt% from the viewpoint of stability of the aqueous dispersion element, and if it exceeds 2.0 wt%, it leads to a decline in durability to fluffing and washability of the separable fastener obtained in this invention.

In the manufacture of the polyurethane aqueous dispersion element, the carboxyl group introduced into the polyurethane may be neutralized by the tertiary amine completely in the form of a salt, but may also be partially neutralized to leave some free carboxyl groups.

In the manufacture of the polyurethane aqueous dispersion element, it is important to use the tertiary amine to form a salt of the carboxyl groups introduced into the polyurethane. Examples of the tertiary amine are trialkylamines such as trimethylamine, triethylamine, methyl diethylamine and tripropylamine, alkanoldialkylamines such as N,N-dimethylethanolamine, N,N-diethylethanolamine, N,N-di- isopropyl ethanolamine and N,N-dimethylpropanolamine, and dialkanolalkylamines such as N-methyl diethanolamine. Triethylamine is particularly preferred. Tertiary amine salts have less sensitivity to water than alkali metal salts such as lithium, sodium and potassium and they have good water resistance. Consequently, the washability of the separable fastener is good.

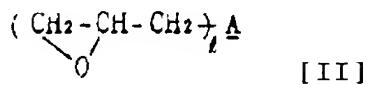
It is desirable to use a chain elongating agent in the manufacture of the polyurethane aqueous dispersion element. Preferred examples of the chain elongating agent are hydrazine or dihydrazines such as adipic acid dihydrazide. Part of the hydrazine or dihydrazide may be replaced by a chain elongating agent normally used in the polyurethane industry, e.g., a glycol such as butane diol or propylene glycol, a diamine such as propylene diamine, ethylene diamine, piperazine, isophorone diamine or xylelene diamine, or water. From the viewpoint of the resistance to fluffing and washability of the separable fastener which is finally obtained, the blending proportion of hydrazine or dihydrazide in the chain elongating agent is at least 10 mole%, preferably 20-100 mole% and more preferably 50-100 mole%.

The manufacture of the aforesaid polyurethane aqueous dispersion element may be carried out according to the normal technique (e.g., Japanese Patent Sho 53-38760). For example, an organic diisocyanate is reacted with polytetramethylene glycol, a carboxyl group-containing compound is reacted to produce a double terminated isocyanate prepolymer containing a carboxyl group, the carboxyl group introduced into this prepolymer is neutralized by a tertiary amine to form a salt and produce a double terminated isocyanate prepolymer, the prepolymer is dispersed in water, and polymerisation is then performed using hydrazine or a chain elongating agent containing hydrazine. Alternatively, the tertiary amine is dissolved in water and

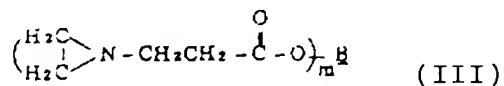
mixed with the aforesaid carboxyl group-containing double terminated isocyanate prepolymer to give a dispersion element. In this process, the use of an organic solvent gives an aqueous dispersion element of smaller particle size, and good water resistance and solvent resistance is obtained when a film is produced from this aqueous dispersion element, but from the viewpoint of safety, hygiene and environmental pollution, it is of course preferable to proceed without the solvent. Hence, although an organic solvent may be used in the manufacture of the aqueous dispersion element, it is preferable that its use is kept to a minimum. Examples of solvents which may be used are acetone, metal ethyl ketone, N-methylpyrrolidone ethyl acetate and dimethylformamide.

In this way, a polyurethane aqueous dispersion element is obtained, and in this dispersion element, the polyurethane may be dissolved or the polyurethane may be colloidally dispersed in water.

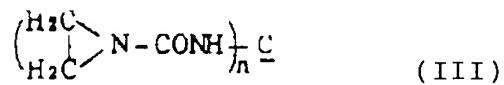
The compound (B) having two or more epoxy rings or aziridine rings in the molecule which is used as a curing agent in this invention is preferably a water-soluble compound represented by the general formula:



a water-soluble compound represented by the general formula:



or a water-soluble compound represented by the general formula:



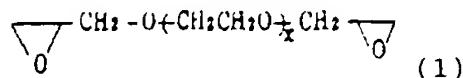
In the formula, A, B are hydrocarbon groups which may contain different atoms, C is an alkane, allylene or arallylene group, and 1, m, n are integers from 2-6 or preferably 2-4. A typical compound is shown below by its

structural formula. The epoxy ring is shown by (  ) and the aziridine

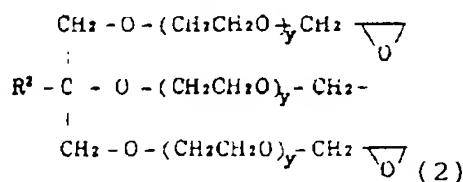
ring is shown by (  ).

For example, the compound shown by the general formula (II) is an

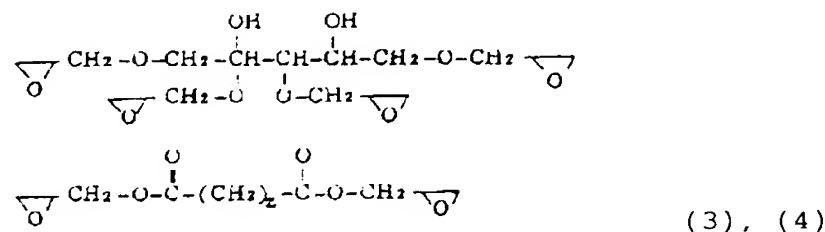
epoxy compound having the structural formulae shown by the following (1)-(5).



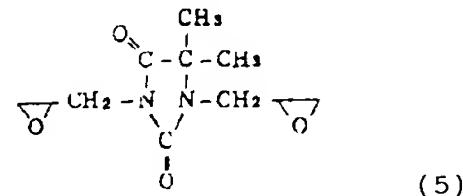
(in the formulae,  $x$  is an integer from 0 to 20).



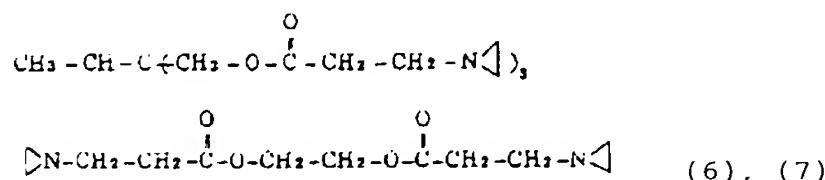
(in the formulae,  $R^2$  is alkyl having 1 to 20 carbon atoms, and  $y$  is an integer from 0 to 20)



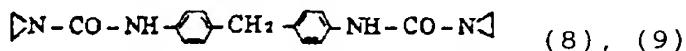
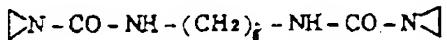
(in the formulae,  $z$  is an integer from 2 to 4)



The compound represented by the general formula (III) is preferably an aziridine compound having the structural formulae shown by the following (6)-(7).



The compound represented by the general formula (IV) is preferably an aziridine compound having the structural formulae shown by the following (8)-(9).



In this invention, the two-solution curing type polyurethane aqueous dispersion is manufactured by mixing the polyurethane aqueous dispersion element (A) with the water-soluble compound (B) having two or more epoxy rings or aziridine rings in the molecule. During this mixing process, or after preparing the two-solution type polyurethane aqueous dispersion element, a suitable amount of a filler, extending agent, thickener, hardening accelerator, antioxidant, ultraviolet deterioration preventing agent or fluorescent agent normally used with this dispersion element, may also be blended.

In this invention, the blending proportion of the polyurethane aqueous dispersion element (A), which is the base resin, with the compound (B) having two or more epoxy rings or aziridine rings in the molecule, which is the curing agent, is 3-25 weight parts, but preferably 5 to 15 weight parts, of curing agent to 100 weight parts of base resin in terms of solids.

It is preferred that in the separable fastener used in this invention, the woven fabric in which the hooks and loops are implanted is manufactured from a synthetic fiber such as polyamide fiber or polyester fiber.

It is preferred that the separable fastener comprising a synthetic fiber such as polyamide fiber or polyester fiber used in this invention is fully degummed or dyed before coating with the aforesaid two-solution curing type polyurethane aqueous dispersion element.

In this invention, the undersurface of the separable fastener may be back coated with the 2 solution curing polyurethane aqueous dispersion element, for example by applying with a roll coater or the like. In this process, the undersurface of the separable fastener may conveniently be coated by impregnating it with the two-solution curing type polyurethane aqueous dispersion element. After coating, the solvent is evaporated to dry the tape, and the curing reaction is allowed to proceed from room temperature to approximately 80-140 °C for a few days, which gives a tape with good performance.

#### Examples

Hereafter, this invention will be described in further detail by means of specific examples and comparative examples, but it is to be understood that the invention is not limited in any way thereby.

In the examples and comparative examples, the durability of the separable fastener to fluffing was measured by fastening and unfastening the hooks and loops 5000 times, and observing the disorder of the pile in the loops. The extent of the disorder was assessed on the following scale.

- 5 - no disorder of the pile whatsoever
- 4 - slight fluffing of the pile in some places
- 3 - slight fluffing of the pile in the whole tape
- 2 - considerable fluffing of the pile in the whole tape
- 1 - severe fluffing of the pile in the whole tape

The resistance to dry cleaning and washability was measured by dry cleaning with Varclean, washing in an automatic washing machine using a synthetic detergent (Super Zab) for 8 hours, and observing the fluffing of the pile by an identical method to that for durability described above.

The compounds used in the examples and comparative examples are shown by symbols, the relation between the symbols and compounds being as shown in the following table.

Table 1

Symbol	Compound
PTG	<u>polytetramethylene glycol</u>
PCL	polycaprolactan glycol
PHA	polyhexamethylene adipate glycol
PEA	polyethylene adipate glycol
PBA	polybutylene adipate glycol
PPG	polypropylene glycol
IPDI	isophorone diisocyanate
HDI	hexamethylene diisocyanate
TDI	tolylene diisocyanate
DMPA	<u>2, 2-dimethylol propionic acid</u>
Et <sub>3</sub> N	Triethylamine
DEAE	diethylamine ethanol
PIP	piperazine
PDA	propylene diamine
HH	hydrazine hydrate
ADH	adipic acid dihydrazide
CR-5L	trifunctional epoxy compound ["CR-5L" (trade name; product by Dainippon Ink & Chemicals, Inc.)]
PZ-33	trifunctional aziridine compound (structural formula (6)) ["PZ-33" (trade name; product by Nippon Shokubai Co., Ltd.)]
HZ-22	bifunctional aziridine compound (structural formula (8)) ["HZ-22" (trade name; product by Nippon Shokubai Co., Ltd.)]

## Example 1

1 mole (1000g) of polytetramethylene glycol (PTG), 3.5 mole (777g) of isophorone diisocyanate (IPDI) and 0.8 mole (107.2g) of 2, 2-dimethylol propionic acid were introduced, 0.1g of dibutyl tin dilaurate was added, and the mixture reacted at 100 °C for 3 hours. The reaction product was cooled to 40 °C, 0.7 mole (70.7g) of triethylamine was added, the mixture was strongly stirred for 10 minutes, and then dispersed by stirring while gradually adding 3 liters of water. Next, after leaving for 5 minutes, an aqueous solution obtained by dissolving 0.68 mole (34g) of hydrazine hydrate (HH) and 0.935 mole (181.4g) of piperazine (PIP) in 0.3 liters of water was added over 5 minutes, and stirring was continued for approximately two hours so as to obtain a polyurethane aqueous dispersion element.

35g of a trifunctional epoxy compound (CR-5L) was added to 1000g of this polyurethane aqueous dispersion element, and mixed thoroughly. The mixed solution thus obtained was used to coat a separable fastener by means

of a roll coater, and its performance was evaluated. The results are shown in Table 3.

From the above table, it is clear that the separable fastener obtained had excellent durability to fluffing, washability and resistance to dry cleaning.

#### Examples 2-5 and Comparative Examples 1-6

A polyurethane aqueous dispersion element was manufactured using the starting materials shown in Table 2, and a two-solution curing type polyurethane aqueous dispersion element was manufactured by an identical method to that of Example 1 except that this aqueous dispersion element and the curing agents shown in Table 2 were used in the proportions shown in Table 2. A separable fastener was manufactured using this dispersion element, and its performance shown in Table 3.

Table 2

		Base resin	Tertiary amine (molar ratio)	Chain elongating agent (molar ratio)	Curing agent	Base resin/curing agent	
Example 1	Polymer diol; average molecular weight (molar ratio) PTG; 1000 (1)	Organic diisocyanate (molar ratio) IPDI (3.5)	Carboxyl group-containing compound (molar ratio) DMPA (0.8)	Et <sub>3</sub> N (0.7)	HH (0.68) PIP (0.935)	CR-5L	100/8
Example 2	PTG; 850 (1)	IPDI (3.0)	DMPA (0.7)	Et <sub>3</sub> N (0.6)	HH (0.52) PIP (0.65)	CR-5L	100/8
Example 3	PTG; 650 (1)	TDI (2.5)	DMPA (0.5)	Et <sub>3</sub> N (0.5)	HH (0.4) PDA (0.6)	CR-5L	100/10
Example 4	PTG; 1500 (1)	HDI (3.0)	DMPA (0.8)	DEAE (0.7)	ADH (0.48) PIP (0.62)	PZ-33	100/8
Example 5	PTG; 2000 (1) PCL; 2000 (1)	TDI (3.0) IPDI (3.0)	DMPA (0.9) DMPA (0.9)	Et <sub>3</sub> N (0.8) Et <sub>3</sub> N (0.8)	HH (1.05) PIP (1.05)	HZ-22 CR-5L	100/8 100/8
Comparative Example 1	PHA; 2000 (1)	IPDI (3.0)	DMPA (0.9)	Et <sub>3</sub> N (0.8)	PIP (1.05)	CR-5L	100/8
Comparative Example 2	PEA; 2000 (1)	IPDI (3.0)	DMPA (0.9)	Et <sub>3</sub> N (0.8)	PIP (1.05)	CR-5L	100/8
Comparative Example 3	PBA; 2000 (1)	IPDI (3.0)	DMPA (0.9)	Et <sub>3</sub> N (0.8)	PIP (1.05)	CR-5L	100/8
Comparative Example 4	PPG; 2000 (1)	IPDI (3.0)	DMPA (0.9)	Et <sub>3</sub> N (0.8)	PIP (1.05)	CR-5L	100/8
Comparative Example 5	PTG; 4000 (1)	IPDI (3.0)	DMPA (0.9)	Et <sub>3</sub> N (0.8)	PIP (1.05)	CR-5L	100/8
Comparative Example 6							

Table 3

	Durability to fluffing		Washability		Resistance to dry cleaning	
	Score	Result	Score	Result	Score	Result
Example 1	5	◎	5	◎	5	◎
Example 2	5	◎	5	◎	5	◎
Example 3	5	◎	5	◎	5	◎
Example 4	5	◎	5	◎	5	◎
Example 5	5	◎	5	◎	5	◎
Comparative Example 1	3-4	△	2-3	×	3-4	△
Comparative Example 2	3	△	2-3	×	3	△
Comparative Example 3	2	×	2	×	2	×
Comparative Example 4	2	×	2	×	2	×
Comparative Example 5	1-2	×	1	×	1	×
Comparative Example 6	4	○	3-4	△	3	△

Results ◎ Very good

○ good

△ fair

× poor

Effect of the Invention

According to the manufacturing method of this invention, a highly durable separable fastener is obtained with excellent resistance to fluffing, washability and dry cleaning, very little fraying of the pile even after long periods of use and practically no change in appearance. Moreover, this manufacturing method presents no problem with regard to safety, hygiene or environmental pollution.

Applicant: Kuraray Co., Ltd.

Agent: Patent Attorney Katashi HONDA